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Studies on the zeolites. Part VI. Edingtonite.[1]

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[Read June 15, 1933.]

THE very rare barium zeolite edingtonite was described by W. Haidinger (1825), and named in honour of Mr. Edington. Haidinger's material consisted of small crystals on thomsonite from Dumbartonshire. An analysis by E. Turner indicated a calcium aluminosilicate, but there was a loss of 11·22 %. The crystals (sp. gr. 2·71) were morphologically tetragonal, with the prism $m(110)$ and sphenoids $p(111)$ and $n(1\bar{1}2)$, and an axial ratio $c/a = 0{\cdot}6725$. A. Breithaupt (1832) gave the name 'Antiëdrit' on account of this symmetry.

M. F. Heddle (1855) examined material from Old Kilpatrick, and showed it was a barium zeolite. His analysis was not very good; it suggested the formula $BaAl_2Si_3O_{10}.3H_2O$, which has been generally adopted, but is not quite correct. The only other analysis in the literature is one by G. Lindström (1896) of material from Böhlet, Westergotland, Sweden. This agrees with the Old Kilpatrick material in composition, but there have been doubts about their identity, for O. Nordenskjöld (1895) showed that the Böhlet material is orthorhombic and optically biaxial, whereas A. Des Cloizeaux

[1] Part V. Mesolite. Min. Mag., 1933, vol. 23, p. 421.

(1862) had described Old Kilpatrick edingtonite as uniaxial negative. Although A. Lacroix (1896) and H. Sjögren (1906) showed that the Old Kilpatrick crystals are really biaxial, and explained their pseudo-uniaxial behaviour as due to complex twinning on m(110), these doubts have persisted to some extent.

In order to make quite certain that the Böhlet material really is true edingtonite, Mr. F. A. Bannister has taken X-ray rotation photographs of cleavage fragments from a Böhlet specimen (B.M. 81049) and an Old Kilpatrick specimen (B.M. 26607). The photographs were identical except as regards the axial ratio. While the Böhlet material is distinctly orthorhombic, having cell sides a 9·56, b 9·68, c 6·53 Å. (all $\pm$ 0·02 Å.), no departure of the Old Kilpatrick material from tetragonal symmetry could be detected by Lauegrams or rotation photographs. The cell size of the Old Kilpatrick material is a 9·585, b 9·585, c 6·53 Å. (all $\pm$ 0·02 Å.). Since optical study shows that the Old Kilpatrick material is also biaxial, and the X-ray photographs are identical save for the difference of axial ratio, we conclude that the Böhlet material is indeed true edingtonite. The difference is probably due to the higher calcium content of the Old Kilpatrick crystals.

None of the material available was suitable for goniometric study. The Old Kilpatrick material was studied by W. Haidinger (1825) who found it to be tetragonal with $c/a = 0{\cdot}6725$, while H. Sjögren (1906) found $c/a = 0{\cdot}6793$, in better agreement with the X-ray value, 0·681. The Böhlet material was studied by O. Nordenskjöld (1895), who found $a : b : c = 0{\cdot}9872 : 1 : 0{\cdot}6733$, and by H. Sjögren (1906), who found $a : b : c = 0{\cdot}9867 : 1 : 0{\cdot}6743$; the X-ray value is 0·988: 1 : 0·675.

W. H. Taylor and R. Jackson (1933) have made a complete crystal-structure analysis of edingtonite. Assuming the mineral is orthorhombic, they find the space-group D_2^3, a result which Mr. Bannister's photographs confirm. Mr. Bannister has also found that with Böhlet material, the intensity of (hk0) diffractions is less than that of (kh0) diffractions; but (hkl) and (khl) diffractions are of equal intensity, except for high orders, for which those for (hkl) are the more intense. Mr. Bannister has also confirmed the relative intensities tabulated by Taylor and Jackson. The structure is based on $(Al_2Si_3O_{10})''$ strings similar to those present in thomsonite and natrolite, but linked together differently. It may be of interest to note that while in natrolite, mesolite, and scolecite, the strings (which are polar) are probably all arranged with their similar ends pointing

in the same direction, the presence of two-fold screw-axes parallel to a and b in the edingtonite space-group requires either that half the chains point in the opposite direction to the other half, as they probably do in thomsonite, or that the chains of edingtonite are not polar, or that the crystal is not truly orthorhombic, but really monoclinic. The last possibility is supported by the optical anomalies observed by H. Sjögren (1906) and O. Nordenskjöld (1895). Dr. W. A. Wooster, of Cambridge, has kindly examined edingtonite for pyroelectricity, and found a distinct effect, indicating the absence of a centre of symmetry.

The amount of Old Kilpatrick material available for study was insufficient for chemical analysis, and little could be done beyond the X-ray work. Optical examination of several fragments showed that the crystals are biaxial negative, with a small optic axial angle, 2E varying from 15 to 20° in different fragments. Twinning on $m(110)$ was observed in one fragment. The refractive indices, α 1·542, β and γ 1·550 ($\pm$ 0·002) are distinctly different from those of the Böhlet material, the birefringence being less. Differences in composition appeared the most likely explanation of the optical and dimensional differences between the Böhlet and Old Kilpatrick edingtonites, though the complete analyses reveal no such differences. But Heddle's analysis (1855) of Old Kilpatrick material showed a loss of over 1 %; and he mentions another partial analysis which showed 6·22 % CaO. The specimen studied optically and by X-rays (B.M. 26607) was therefore examined micro-chemically for calcium, which was found to be present in appreciable amount. As calcium is only present in very small amounts in the Böhlet material, it seems reasonable to attribute the optical and dimensional differences to its presence.

The Böhlet edingtonite was employed for the remainder of the present work. A chemical analysis was made (table I*a*) and is compared with Heddle's and Lindström's analyses in table I*b*. The number of oxygen atoms per unit cell was calculated from the cell-size, analytical and density figures as usual, and shown to be 20. Calculating the analyses on this basis, it is clear that the commonly accepted formula is correct except for the water. The vapour-pressure study shows that the air-dry material has a water-vapour pressure equal to the partial pressure of the water-vapour in the air, and on exposure to higher water-vapour pressures, more water is taken up; saturation of the zeolite is, however, reached before the

saturation pressure for liquid water. The unit cell formula of fully-hydrated edingtonite is $Ba_2Al_4Si_6O_{20}.8H_2O$.

TABLE I*a*. New chemical data on air-dry edingtonite from Böhlet, Sweden (B.M. 81049). Material used for main analysis 0·4422 gram, for alkalis 0·2227 gram.

SiO_2.	Al_2O_3.	BaO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Oxygen.
35·35	19·98	30·83	0·10	0·04	0·65	13·11	100·06	31·59 %

TABLE I*b*. New and old analyses of edingtonite, calculated to unit-cell contents (atomic ratios on an assumed basis of 20 oxygen atoms). Also the oxygen atoms per unit cell, calculated from the analyses and specific gravities and the unit-cell dimensions.

	1.	2.	3.
Si	5·94	6·01	5·96
Al	4·29	3·94	3·97
Ba	1·67	1·96	2·03
Ca	trace	0·03	0·02
Na	trace	0·08	0·01
K		0·07	0·14
H_2O	6·68	7·23	7·37
Si + Al	10·23	9·95	9·93
Kations	1·67	2·14	2·20
Class of analysis *	C.	A.	B.
Sp. gr.	2·694	2·782	2·777
Oxygen, atoms per unit cell	20·8†	20·33	20·08

1. M. F. Heddle, 1855. Old Kilpatrick, Dumbartonshire.
2. G. Lindström, 1896. Böhlet, Sweden.
3. B.M. 81049, Böhlet.

* See Part II of this series for the method of classification used.

† The cell size determined for the Böhlet material was used for all three analyses, since Heddle's shows only traces of lime. If the cell size determined for the calciferous Old Kilpatrick specimen is used for Heddle's analysis, the oxygen content comes to 20·7 atoms per unit cell.

Optical study of the Böhlet edingtonite gave results in good agreement with those of O. Nordenskjöld (1895) and H. Sjögren (1906). The negative Bx_a is perpendicular to *c* (001), and the axial plane parallel to *b* (010). The refractive indices, optic axial angle (2V), and birefringence ($\gamma - \beta$) were determined for a series of wave-lengths; the results are given in tables II and III and shown graphically in fig. 1. The accuracy of the optical measurements was checked by comparing the measured values in the same manner as was done for natrolite.[1] These figures are all for air-dry material, with 7·4 mol.

[1] Part III of this series, Min. Mag., 1932, vol. 23, p. 243.

H_2O per unit cell. For fully hydrated edingtonite, the refractive indices would probably all be appreciably higher.

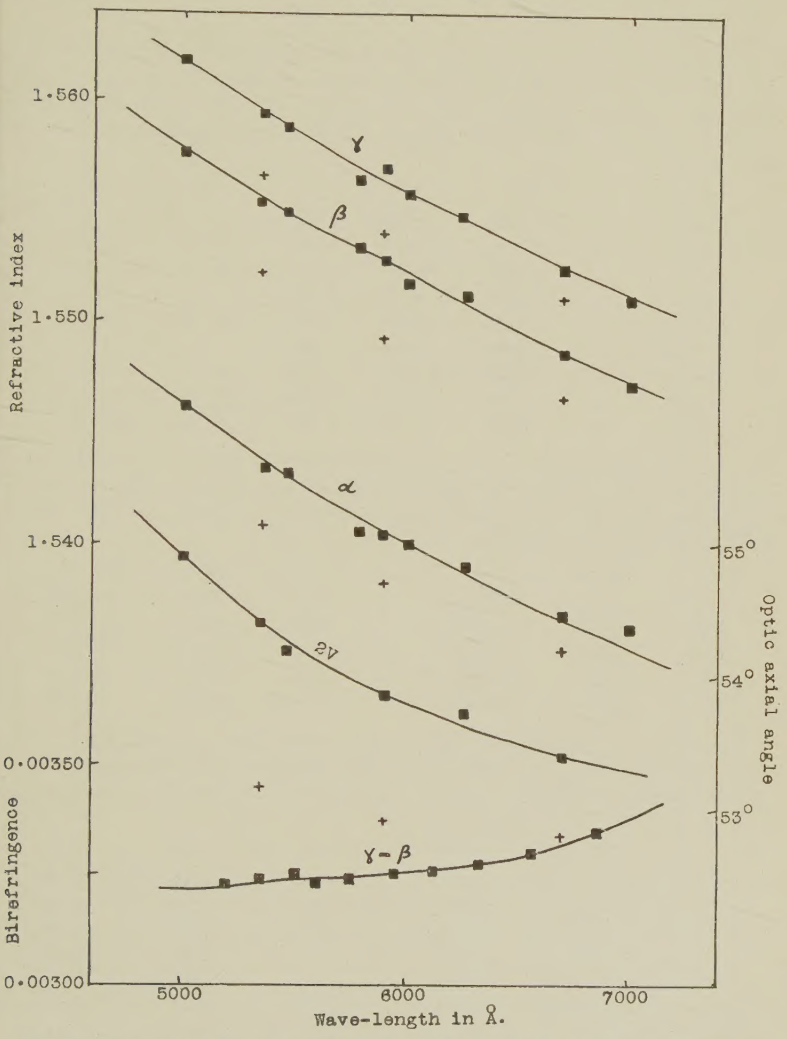

FIG. 1. The variation of the refractive indices, optic axial angle, and birefringence of edingtonite from Böhlet (B.M. 81050) with the wave-length of the light. The small crosses show the results of O. Nordenskjöld (1895) for α, β, γ, and 2V.

The only published dehydration data on edingtonite appear to be determinations of the water loss at 100° C. and 230° C. by G. Lind-

ström (1896); at the former temperature, 5·12 mols. water per unit cell are left, and at the latter 2·87 mols.[1] The lost water is wholly recovered in moist air.

TABLE II. Refractive indices and optic axial angles of air-dry (7·37 mol. H_2O per unit cell) Böhlet edingtonite (B.M. 81050), for light of various wave-lengths. Maximum probable error in the refractive indices $\pm 0{\cdot}0010$, mean probable error $\pm 0{\cdot}0005$; 2V $\pm 10'$. The column $\gamma - \alpha$ is calculated from the measured values of β, $\gamma - \beta$, and 2V.

λ(Å.).		α.	β.	γ.	2V.	γ−α calc.
7000	...	1·5362	1·5471	1·5510	—	—
6708	...	1·5368	1·5487	1·5525	53° 24′	0·0165
6250	...	1·5390	1·5513	1·5548	53 44	0·0161
6000	...	1·5401	1·5517	1·5559	—	—
5893	...	1·5405	1·5528	1·5569	53 52	0·0158
5780	...	1·5405	1·5534	1·5565	—	—
5461	...	1·5433	1·5549	1·5589	54 12	0·0155
5350	...	1·5435	1·5553	1·5594	54 24	0·0154
5000	...	1·5461	1·5576	1·5618	54 54	0·0152

TABLE III. Birefringence ($\gamma - \beta$) of air-dry (7·37 mol. H_2O per unit cell) Böhlet edingtonite (B.M. 81050), for light of various wave-lengths. Determined as extinctions in several orders, on a plate of thickness 6·76 mm., $\perp c(001)$. Maximum probable error, $\pm 0{\cdot}00002$.

Order.	λ(Å.).	γ−β.	Order.	λ(Å.).	γ−β.
33rd	6860	0·00335	38th	5770	0·00325
34th	6570	0·00330	39th	5600	0·00323
35th	6330	0·00328	40th	5500	0·00325
36th	6120	0·00326	41st	5350	0·00324
37th	5950	0·00326	42nd	5200	0·00323

TABLE IV. The constants of the vapour-pressure surface of edingtonite from Böhlet (B.M. 81049). Heat of hydration, Q, in calories, and integration constant, A, of the equation $\log_{10} p = A - Q/(RT\log_e 10)$, for various water contents per unit cell, c.

c.	Q.	A.	c.	Q.	A.
8·0	$1{\cdot}08 \times 10^4$	9·00	5·4	$1{\cdot}73 \times 10^4$	10·30
7·7	1·14	9·25	4·7	1·91	10·38
7·4	1·28	9·62	4·15	2·10	10·42
7·15	1·36	9·84	3·5	2·26	10·47
6·8	1·44	10·00	2·8	2·48	10·50
6·4	1·55	10·08	2·4	2·59	10·52

Measurements of the vapour-pressure surface of edingtonite have been made and interpreted by the methods described in previous

[1] These figures are in good agreement with the author's vapour-pressure work. At 100° C. and about 1 mm. Hg water-vapour pressure, about 5·0 mols. water per unit cell should be left, while at 230° C. and 1 mm. Hg, the residual water should be about 2·8 mols.

papers in this series. The experimental values of Q and A, the vapour-pressure constants, are given in table IV and fig. 2, while the isohydric curves are shown in fig. 3. At 15° C. the water-vapour pressure of fully hydrated edingtonite is 7 mm. Hg, so that edingtonite

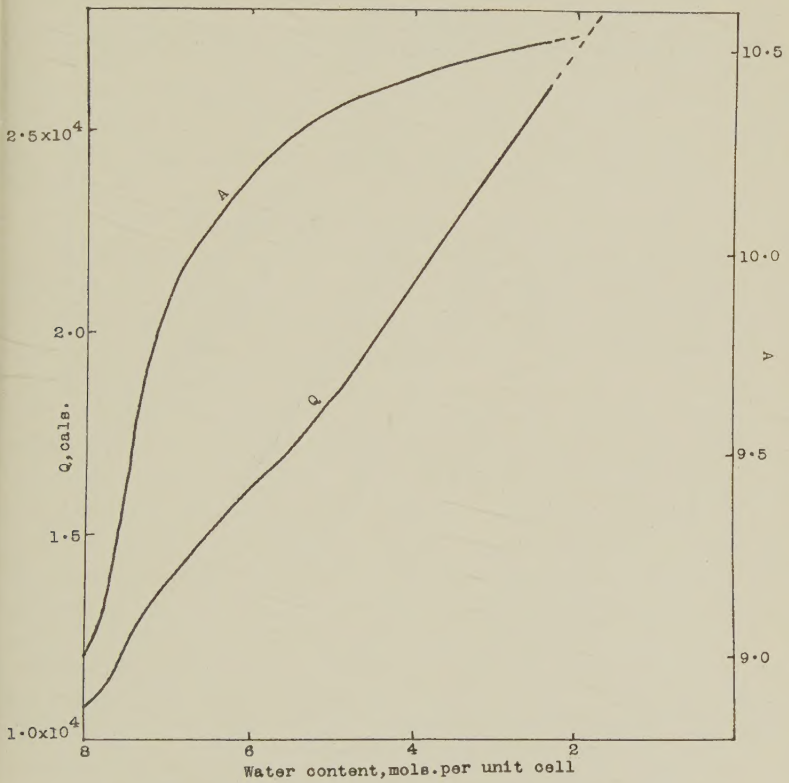

FIG. 2. The constants of the vapour-pressure surface of edingtonite from Böhlet (B.M. 81049). Heat of hydration, Q, in calories, and integration constant, A, of the equation $\log_{10}p = A - Q/(RT\log_e 10)$, for various water contents per unit cell, c.

kept in dry air ($p_{H_2O} < 1$ mm. Hg) loses a very appreciable amount of water—up to 1 to 1½ %. There are no breaks or discontinuities in the vapour-pressure surface of edingtonite, indicative of other modifications or lower hydrates.

Owing to shortage of material, the variation of the optical properties of edingtonite during dehydration could not be studied in detail, but the material removed from the vapour-pressure apparatus

was examined by the immersion method. The results could not be made very accurate, as the dehydrated zeolite very rapidly absorbs water-vapour from the air, the crystals (previously clear and but little shattered) decrepitating markedly in moist air.[1] The crystals,

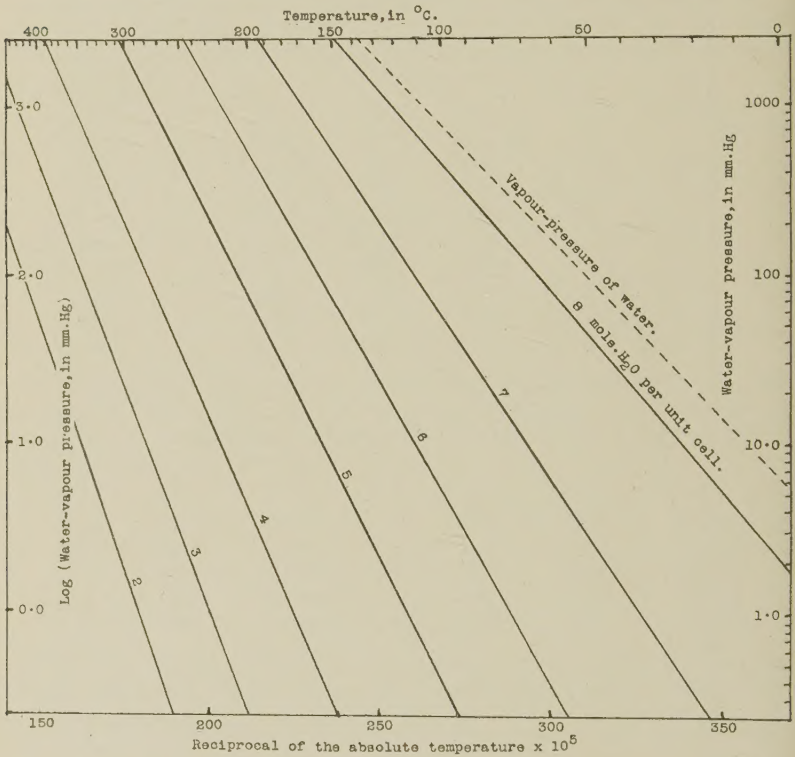

FIG. 3. Isohydric vapour-pressure curves for edingtonite from Böhlet (B.M. 81049).

which contained 2·4 mols. H_2O per unit cell, had negative elongation ($a = c$), moderate birefringence, and α 1·544. This is higher than for edingtonite with 7·37 mol. H_2O per unit cell. It is probable that, as with the other zeolites so far studied, the refractive indices first fall, then rise again with progressive dehydration. Nordenskjöld's data support this conclusion, for his refractive indices are consistently lower than the author's, while Lindström's analysis shows less water.

[1] It is possible that absorption of air may also be involved, since the material had been dehydrated in vacuo.

The heat of hydration of edingtonite was determined directly, by the same method as was used for natrolite and mesolite, as a check on the vapour-pressure work. With 2·06 grams edingtonite, dehydrated to a loss of 0·204 gram water (leaving 2·4 mol. per unit cell), a temperature rise of 4·5° C. (corrected to zero time) was observed, with a water-equivalent of 16·68 grams. The heat evolution continued during 6 minutes. From these data the mean heat of hydration of edingtonite by water-vapour, over the range 2·4 to 8·0 mol. H_2O per unit cell, is 17,000 cals. per gram-mol. of water reacting. The value deduced from the vapour-pressure experiments is 18,000 cals.

A few base-exchange experiments were carried out on the material which had been used for the vapour-pressure work and for the heat of hydration. Fusions of sodium chlorate, potassium thiocyanate, silver and thallous nitrates all gave considerable reaction. The products were analysed and examined optically and by X-rays, with results given in table V (p. 492).

The thallium compound was somewhat contaminated with thallous iodide and with barium sulphate, but apart from these impurities appeared to be homogeneous. Its X-ray rotation photograph showed that the unit cell is somewhat larger than that of the parent substance, and more nearly tetragonal. There were marked changes in the intensity of many diffractions, but there can be no doubt that the material is essentially an edingtonite. The very high refractive index and density are of course due to the high thallium content.

The silver compound was brownish in colour, probably owing to free silver oxide, but appeared quite homogeneous. An X-ray photograph was very weak, despite long exposure, indicating that the structure has probably broken down to a considerable extent, but it appears to be essentially silver-edingtonite.

The action of potassium thiocyanate yielded a product contaminated with barium sulphate, but otherwise homogeneous. Its unit cell is eight times as large as that of edingtonite, each dimension having been doubled, or rather slightly more than doubled. Hence it can no longer be classed as an edingtonite, and may be called potassium pseudo-edingtonite. The odd layer lines on the rotation photograph of this compound are very weak, the unit cell is face-centred, and there is a very close resemblance to the edingtonite photograph, indicating that the anionic $(Si,Al)O_2$ framework remains unaltered.

TABLE V. Base-exchange data for Böhlet edingtonite. The material (B.M. 81049) was treated for 96 hours with salt fusions, thoroughly leached, and examined air-dry. The untreated material had α 1·541, β 1·553, γ 1·557 for Na-light, and cell sides a 9·56, b 9·68, c 6·53 Å.; for its composition see tables I a and I b.

Salt used ...		...	$TlNO_3$.	$AgNO_3$.	$NaClO_3$.	KCNS.
Temperature		...	270°.	270°.	270°.	220° C.
Percentage composition ...	SiO_2	...	16·85	31·76	42·25	31·46
	Al_2O_3	...	9·62	18·84	24·60	19·29
	BaO	...	2·38	10·75	16·46	5·99
	R_2O*	...	44·73	35·66	8·79	[15·35] ‖
	H_2O	...	4·22	2·07	7·55	5·89
	Total	...	[100·00]†	99·74‡	100·32§	[100·00]¶
Oxygen, %** ...		...	19·85	29·64	38·23	37·28
Atoms per 20 oxygen ...	Si ...	...	5·82	5·76	5·92	5·76
	Al ...	...	3·92	4·03	4·05	4·17
	Ba ...	...	0·32	0·76	0·90	0·43
	R* ...	...	4·37	3·35	2·38	3·59
	H_2O	...	4·87	1·25	3·52	3·60
Sp. gr., calc. ...		...	4·03	3·13	2·56	2·21 ‖‖
Sp. gr., found ...		...	4·2±	3·2	2·50§§	2·47
Refr. index (Na-light)	α'	...	1·710††	1·645††	1·518	1·547
	γ'				1·525	1·555
Optic orientation; elongation		...	positive	positive	positive	negative
Cell sides in Å.‡‡	a ...	...	9·94	9·36	19·03	19·46
	b ...	...	10·00	9·36	19·03	20·04
	c ...	...	6·65	6·5	11·90	13·17
	r* ...	...	1·7?	1·5?	0·98	1·33
Water retained at 300° C., mols. per 20 oxygen		...	3·32	0·73	0·85	1·39

* R is the portion of the salt employed in the base-exchange, and r its radius in Å. The radius of $Ba^{\cdot\cdot}$ is about 1·31 Å. (W. H. Zachariasen, 1931).

† Including 10·98 % $BaSO_4$ and 11·22 % TlI (by difference), impurities.

‡ Including 0·66 % $BaSO_4$, impurity.

§ Including 0·47 % $BaSO_4$, impurity.

‖ By difference.

¶ Including 22·02 % $BaSO_4$, impurity.

** Calculated after deduction of impurities.

†† Birefringence very weak. Probable accuracy ±0·010.

‡‡ Probable accuracy, ±0·02 for Tl, ±0·04 for Na and K, ±0·04 (?) for Ag derivatives.

§§ Probable accuracy, ±0·05; hence, oxygen per unit cell, 156±3·5 atoms.

‖‖ Some of the $BaSO_4$ is included in the zeolite. If it were all included, the calculated sp. gr. would become 2·71. The figure of 2·21 corresponds to the zeolite free from inclusions.

By the action of sodium chlorate, a homogeneous product was obtained which gave a weak X-ray photograph. The unit cell has approximately doubled in each direction, compared to edingtonite, but unlike the potassium compound the odd layer-lines are not weak, and there is one very weak diffraction, (321), which does not correspond to a face-centred cell. Moreover, the c spacing is considerably less than twice that of edingtonite, whereas in all the base-exchange products of zeolites based on $(Al_2Si_3O_{10})''$ strings so far examined the dimension parallel to the strings is but little affected during base-exchange. The compound is provisionally classed as sodium pseudo-edingtonite, corresponding to the potassium compound; it would undoubtedly repay further study, but time did not permit of this.

All of these base-exchange products differ optically and in their X-ray photographs from the corresponding derivatives prepared from thomsonite or from any of the members of the mesotype group—natrolite, mesolite, and scolecite. Hence the structures must be different, the base-exchange work thus affording confirmation of the structural study of W. H. Taylor and R. Jackson (1933).

The synthesis of barium zeolites, supposed to be edingtonite, has twice been described. J. Lemberg (1876) treated potassium-natrolite with barium chloride, and obtained a compound of composition near that of edingtonite. But as natrolite and edingtonite differ structurally, this must have been a barium-natrolite, not an edingtonite, unless the zeolite had passed into solution and recrystallized. O. C. Magistad (1929) prepared a barium aluminosilicate by treating with barium chloride the precipitate obtained on mixing sodium silicate and sodium aluminate solutions. A 'concentrated water extract' of this barium compound was set aside, and 'several months later small crystals 1–4 mm. long were discovered, which upon analysis . . . were found to be eddingtonite' [*sic*]. This identification is hardly conclusive, and it would seem probable that an artificial production of edingtonite has yet to be performed.

Summary.

Edingtonites from Old Kilpatrick and from Böhlet have been shown to be essentially identical, small differences being due to an appreciable calcium content in the former. The unit-cell formula of edingtonite is $Ba_2Al_4Si_6O_{20}.8H_2O$. The cell dimensions have been determined for both Old Kilpatrick and Böhlet material which differ

appreciably. In both cases there is good agreement between the goniometric and X-ray axial ratios. The optical properties of both Old Kilpatrick and Böhlet material have been studied. A new analysis of the latter gives results in agreement with the above formula. The vapour-pressure of Böhlet edingtonite has been determined at various temperatures and degrees of hydration, and checked by a direct determination of the heat of hydration. By base-exchange, thallous- and silver-edingtonites have been prepared, and also potassium and sodium compounds (pseudo-edingtonites), which have a unit cell approximately eight times as large as that of edingtonite. None of these products is identical with the corresponding base-exchange products from the mesotypes or from thomsonite, in conformity with their essentially different structures.

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On the accuracy of mineralogical measurements.

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[Read June 15, 1933.]

ALMOST any scientific periodical devoted to mineralogy will afford examples of the failure on the part of some workers to realize the limitations of the accuracy of their measurements. Often results are calculated to far more places of decimals than the measurements can possibly warrant. In other instances measurements which show differences quite outside the limits of probable error are regarded as being in good agreement; this last failing applies especially to chemical analyses, which occasionally provide decided evidence against the formula they are supposed to support.

The accuracy of goniometric measurements is, of course, very variable, but only in rare cases does it reach 1′, and even the most perfect crystals probably could not be relied on beyond $\frac{1}{4}'$; in the great majority of cases, diffuse reflections and vicinal growth lower the accuracy, and 5–10′ is the probable accuracy of most goniometric measurements. A glance at a table of natural tangents will show that in the most favourable case, where the measurement is of an angle of the type $c(001):r(101)$ in the orthorhombic or a more symmetrical system, the probable error in the axial ratio for values of the measured angle between 45° and 60° is of the order of $\pm 0{\cdot}0005$ per 1′ error in the measurement; with increase in the measured angle, the error in the axial ratio falls, to about $\pm 0{\cdot}0003$ per 1′ with an angle of 80°; on the other hand, an angle of 30° implies an error of $\pm 0{\cdot}0011$ per 1′ error in the measurement. In the monoclinic and anorthic systems the probable accuracy of the axial ratio is somewhat less since several angles, all liable to error, are needed to compute the ratio. On the other hand, if several extra measured angles are taken into account by a suitable method of adjustment, the probable accuracy of the axial ratios is somewhat

enhanced. T. V. Barker[1] strongly advised such a procedure wherever it can be carried out without much additional labour, and by its application to first-class material, the accuracy of the axial ratios could probably be made about $\pm 0{\cdot}0001$. Crystals as perfect as some of those grown by A. E. H. Tutton might occasionally justify the computation of an axial ratio to the fifth decimal place, with a probable error of say $\pm 0{\cdot}00003$, but the accuracy of the average crystallographic measurement cannot possibly justify the publication of axial ratios to six or seven places of decimals, as has been done from time to time. Indeed, the accuracy of the axial ratios deduced from most goniometric work is probably of the order of $\pm 0{\cdot}002$–$0{\cdot}005$, and really only justifies three places of decimals in the axial ratios. While the writer would not suggest that the time-honoured practice of computing axial ratios to four places of decimals be dropped, it is important that it should be more generally recognized that the fourth place is, as a rule, superfluous.

Refractive index determinations by the immersion method are frequently accompanied by a statement of the probable maximum error, but there is often a tendency to over-estimate the accuracy of determinations by the prism method. Assuming that a good well-polished prism is cut, the angle of the prism can generally be obtained accurate to $\frac{1}{2}'$, but only rarely can the angle of minimum deviation of the refracted light be obtained closer than $1'$, and often the accuracy is less.

It is a simple matter to determine the error in the refractive index, n, consequent on given errors in the measurement of the prism angle, A, and the angle of minimum deviation, D. From the well-known equation $n = \sin(A+D)/2/\sin(A/2)$ we have by differentiation with respect to A and to D: $dn/dA = -\frac{1}{2}\sin\frac{D}{2}\operatorname{cosec}^2\frac{A}{2}$, and $dn/dD = \frac{1}{2}\left(\cos\frac{D}{2}\cot\frac{A}{2} - \sin\frac{D}{2}\right)$, A and D being measured in radians. These equations show that the error in n consequent on a given error in A increases with increase of n and, very rapidly, with decrease of A, while the error consequent on a given error in D decreases with increase of n, but increases considerably with decrease of A.

A few probable errors calculated from the above equations are collected in table I. From this table it will be seen that, taking

[1] T. V. Barker, Graphical and tabular methods in crystallography. London, 1922, p. 100.

both sources of error into account, a refractive index determination by the prism method is subject to errors which depend only very slightly on the magnitude of the refractive index, but markedly on the angle of the prism used, increasing very rapidly as the prism angle decreases. Only with a good prism of reasonably large angle is a fourth place justified in a refractive index measured by the prism method. Where duplicate measurements differ by 5′ (which often happens), or where a prism of as small an angle as 20° has to be used for any reason, three places of decimals only can justly be given. Very rarely can a fifth place of decimals be taken seriously, and since an error of 1″ in each of the two measurements means 0·000006 in the refractive index a sixth decimal place is invariably worthless except in very highly specialized investigations.

TABLE I. The errors in a refractive index determination by the prism method consequent on an error of $\pm\frac{1}{2}'$ in the determination of the prism angle, A, on an error of $\pm 1'$ in the angle of minimum deviation, D, and on both errors jointly, calculated for various values of A and of the refractive index, n.

A.	n.	δn for $\delta A=\frac{1}{2}'$.	δn for $\delta D=1'$.	δn for $\delta A=\frac{1}{2}'$ and $\delta D=1'$.
60°	1·4	0·00007	0·00021	0·0003
	1·5	0·00009	0·00019	0·0003
	1·75	0·00015	0·00015	0·0003
30°	1·5	0·00035	0·00038	0·0007
20°	1·5	0·00079	0·00076	0·0015

The decrease in accuracy of a refractive index determination when small-angled prisms are used is clearly shown by the experiments of M. Kołaczkowska,[1] which agree closely with the above figures. The advantages of a large-angled prism are somewhat discounted by the decrease in the amount of light falling on the prism, as pointed out by Kołaczkowska, and also by the increased reflection at the prism faces, and the increased effect of imperfections in the refracting faces, so that the most accurate results will in general be obtained with prisms of angle considerably smaller than the largest-angled prism which will pass light in the ' minimum deviation ' position.

The accuracy of the total-reflection method for refractive indices has been discussed in detail by F. Schwietring,[2] who states that an

[1] M. Kołaczkowska, Arch. Prac. Min. Tow. Nauk. Warszawa, 1926, vol. 1, p. 9. [Min. Abstr., vol. 3, p. 321.]

[2] F. Schwietring, Zeits. Krist., 1930, vol. 75, p. 449 and vol. 76, p. 87, [M.A. 4–447]. W. Geffcken and H. Kohner (Zeits. Physikal. Chem., 1928, Abt. B,

accuracy of $\pm 0{\cdot}0002$ can be obtained, but it does not seem likely that many determinations will approach this figure.

Birefringence measurements always involve a determination of thickness of the plate used, and since there is no difficulty in accurately determining the path-difference, it is the accuracy of the thickness measurements that decides the accuracy of the result. Rarely can this exceed 1 %, and in most determinations under the microscope 5 % or even more is the probable error. Yet birefringences, measured apparently under the microscope, are regularly published to three or even four significant figures by some authors without comment, and used for the computation of optic axial angles.

The error in a directly measured optic axial angle can only be found by comparison of successive readings, and may be anything from 1′ or 2′ to several degrees. But since computed optic axial angles are often published to minutes or even half-minutes of arc, it is of some interest to see how far this is justifiable. As above mentioned, direct birefringence measurements will rarely exceed 1 % in accuracy, and if we assume this accuracy in both $\gamma - \alpha$ and $\beta - \alpha$, the accuracy in sinV will also be about 1 %, which means an accuracy of 2V round about 2 % for large angles, improving for small ones; but for small ones, the accuracy in the smaller birefringence is very unlikely to reach 1 %, so that on the whole we may say that the accuracy of an optic axial angle computed from birefringence measurements is never likely to exceed 2 %, and will more often be of the order of 5–10 %. This would justify, in favourable cases, a citation to $\frac{1}{2}°$, but never to minutes of arc. The accuracy of an optic axial angle calculated from refractive index measurements can only be determined for specific instances, since the accuracy of the birefringence data needed will be very variable. But since the refractive indices are not likely to exceed $\pm 0{\cdot}0003$ in accuracy, we can say in general that the accuracy of 2V is likely to be about $0{\cdot}06/B$ %, where B is the smallest birefringence.

Extinction-angles are very difficult to determine accurately and few authors quote them to a nearer approximation than 1°. By taking all the precautions mentioned in the text-books, a further accuracy, up to say 10′, may be attained, perhaps even more in

vol. 1, p. 456, [M.A. **4** 449]) were only concerned with liquids, and the high accuracy they claim could not possibly be extended to measurements on crystals without extraordinary precautions.

favourable cases. One possible source of error which is often neglected, the departure of a section plate from the intended direction by a degree or so, the author has recently discussed in some detail.[1]

While the general tendency seems to be to over-estimate the accuracy of physical measurements on crystals, chemical analyses are often far too lightly valued—perhaps, often, because the mineralogist is not an analyst. Sometimes important analyses are entrusted to inexperienced students, with deplorable results, and the mineralogist bases his conclusions on an analysis which is quite unfit for publication. Both these tendencies are really different aspects of the same thing—a tendency in some quarters to treat the chemistry of a mineral too lightly. The probable accuracy to be expected in a careful analysis of good material by a skilled analyst is discussed in detail by Hillebrand and Lundell.[2] As they point out, the probable accuracy of an analysis varies greatly with the elements to be determined apart from all other factors, but in general terms we may say that with few exceptions[3] the error in the determination of a substance present in amount exceeding 10 % should not greatly exceed 1 % of the amount there. Yet analyses showing silica varying from 37 to 42 % were until recently accepted as in fair agreement with a fixed formula for thomsonite. Silica in analcime ranges, according to the published analyses, from 52 to 56 %, but rarely is any suggestion made that the formula $NaAlSi_2O_6.H_2O$ is inadequate. The formula of pyrite is always given as FeS_2, and few writers mention that an excess or deficit of sulphur well outside the experimental error has been repeatedly shown by analyses. Where the atomic ratios calculated from an analysis depart from the suggested formula by more than about 1–2 %, some explanation is certainly called for.

A similar tendency is found in much X-ray work. With care, the unit cell size should be determined with an accuracy of at least 2–3 %, and a density determination should be more accurate than $\frac{1}{2}$ % as a rule, so that a departure of the molecular cell content from the ideal figure by more than about 3 % should be suspect—indeed $1\frac{1}{2}$ % can usually be attained. Yet there have been instances where 5 % (2·1 for 2) or even greater departures have been accepted without com-

[1] M. H. Hey, Min. Mag., 1933, vol. 23, p. 367.

[2] W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analysis. New York, 1929, pp. 3–6, 874 ff.

[3] Mainly substances determined indirectly, as alumina or ferric iron in rock analyses. Here errors in several major constituents may, in an unfavourable case, fall on one minor constituent.

ment. At best, computation of the number of multiples of a selected ideal formula per unit cell is by no means an ideal practice. It is far better to compute, from an actual analysis of the material, the number of atoms of each kind in the unit cell. Dependence on an ideal formula which may be incorrect is thereby avoided, and the true accuracy of the work revealed. For if the material used does not exactly correspond to the ideal formula taken, by reason of isomorphous replacement or of inaccuracy of the formula, a quite incorrect idea of the accuracy or inaccuracy of the X-ray work may be given.

The statement of specific gravities is often made in an incomplete manner, thereby reducing the available accuracy. Thus 'sp. gr. 3·368 at 20° C.' does not state clearly whether the standard of comparison is water at 20° C. or at 4° C., and as the difference between the two interpretations amounts to 0·0087, it is of some importance. Probably the best method of statement is '$D_4^{20} = 3{\cdot}368$ (or $D_{20}^{20} = 3{\cdot}377$), corrected to vacuum'. The vacuum correction (amounting in the above case to 0·003) is not needed where the measurements only justify a statement of the specific gravity to three significant figures.[1]

One curious tendency which can sometimes give a quite misleading idea of the accuracy of measurements of all kinds is the misuse of decimal notation. Thus when a specific gravity is cited as 4·25, one is never sure whether the probable error is $\pm 0{\cdot}01$, $\pm 0{\cdot}05$, or even $\pm \frac{1}{4}$. Where the probable error is greater than $\pm 0{\cdot}2$, to publish such a figure as 4·25 is most misleading; it should be cited as $4\frac{1}{4}$, which implies a probable error of $\frac{1}{4}$. A statement of hardness as 3·5 or 3·75 merely implies a value approximately midway between 3 and 4 or nearer 4 than 3. Such values should be given as $3\frac{1}{2}$ or $3\frac{3}{4}$.

[1] A. Hutchinson, Min. Mag., 1924, vol. 20, p. 198.

Silica-glass from the Libyan Desert.[1]

By P. A. Clayton, F.G.S.
Inspector, Desert Surveys, Survey of Egypt,
and L. J. Spencer, M.A., Sc.D., F.R.S.
Keeper of Minerals, British Museum.

[Read November 9, 1933.]

Discovery and occurrence (P. A. Clayton).

An occurrence of silica-glass in lumps up to 10 lb. in weight, smaller fragments being scattered over an area at least 80 by 25 kilometres, has been discovered in the course of the work of the Egyptian Desert Surveys. A Survey expedition under Mr. P. A. Clayton was sent out in December 1932 to work in the unexplored area of the Sand Sea and Gilf Kebir, west of Major R. A. Bagnold's 1930 route, and found the glass on December 29, 1932. It occurs lying on the surface of the Nubian sandstone in the sand-free corridors between the high north-south dune ranges of the south-west of the Sand Sea (fig. 1). The largest lumps were found in approximately latitude 25° 25′ N., longitude 25° 30′ E. The district is not easily accessible, as direct travel from Abu Mungar or Dakhla by car is impracticable. Water is only available at Ain Dalla, reached by a winding route some 500 km. long through the Sand Sea, or at Kufara Oasis some 300 km. away in Italian Cyrenaica.

A hurried preliminary reconnaissance has so far not revealed anything in the geology of the district which throws light on the occurrence of the silica-glass, and no crater has been found in the district. Some 30 per cent. of the area is hidden by dune ranges nearly 100 m. high, but the dunes are so regular that it is probable that the surface on which they lie is featureless. The dunes run in parallel north-south ranges 2 to 5 km. apart, steep on the eastern face, with a long soft sand slope on the west, and the underlying Nubian sandstone plain, generally free of sand, has an almost imperceptible slope averaging 1 in 1000 from south to north.

[1] Portions of this paper were published in the Geographical Journal, October, 1933, vol. 82, pp. 375–377.

The surface of this plain in the southern part of the silica-glass area is hard quartzite, overlain in places with reddish sandstone, and also in parts by a reddish alluvial deposit probably derived from weathering of the sandstone. Some of this reddish material can be seen adhering to the specimens of glass which were lying on it. Such specimens were not found more than half embedded, and though holes were dug where the glass lay thickest, none was found below the surface.

Farther north the surface is a coarse quartz gravel, the pebbles of which are very rounded, while the glass shows no signs of having been rolled, though its surface is wind-eroded. As one goes north the gravel becomes finer, till at the northernmost point where glass was definitely found the surface is a thin crust of fine gravel over a white angular quartz sand. Small pieces of clear quartz are common in the gravel, and not easy to distinguish when searching from fragments of glass 3–5 mm. long.

No well-worked tools of silica-glass were found, though a few flakes were certainly made by man. Only two small fragments, in company with a definite artifact of quartzite, were found actually on the sand ridges, and these must have been carried up there and dropped. Near the largest lumps a number of spots were found where groups of fairly large (10 cm.) fragments occur within a square metre, as though a large lump had been broken up. Attempts to fit the pieces together were unsuccessful, possibly due to the way in which the glass flies to pieces on fracture.

The extent of the area over which it is distributed is only vaguely known. None was seen south of the old Kufara to Abu Mungar camel route, and the first pieces were seen about 4 km. north of this, For about 26 km. farther north up the central corridor in which it occurs pieces are visible every few yards, even from a moving car, while farther north one has to stop and search, sometimes for minutes before a single fragment is found. 84 km. north of the old camel road it was only after considerable search that a few tiny fragments were found. The distribution in the adjacent corridors on either side was similar, though the lumps were smaller and less plentiful than in the central corridor, while pieces were also picked up in the next corridors east and west.

About a hundredweight of the silica-glass was collected and brought to Cairo, though more could have been collected if transport were available.

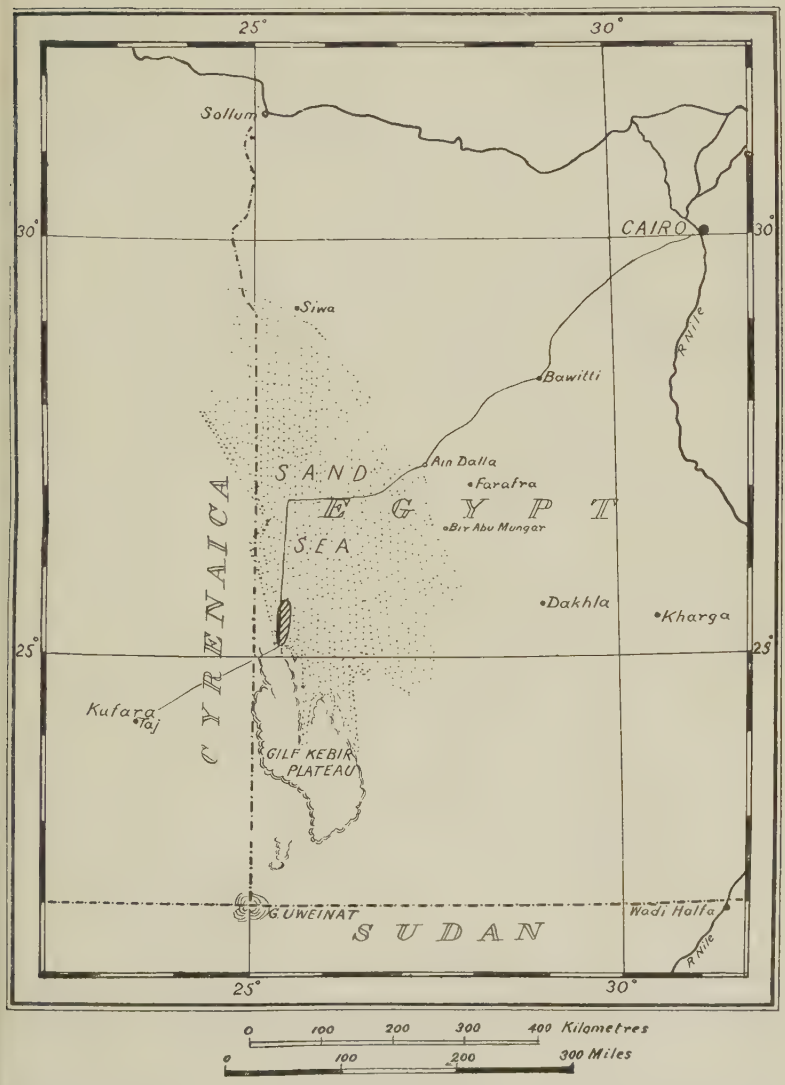

FIG. 1. Sketch-map showing the locality of the silica-glass.

Subsequently sorting over the collection of small pieces, it was surprising to find how many of them (at least 10 %) showed old fractures which might have been produced by an intentional blow (fig. 2). Mr. George Murray and the Rev. P. Bovier-Lapierre were prepared to accept most of these as having been chipped off; but Dr. John Ball and Mr. Brunton, regarding the curved bump as a conchoidal fracture and not a bulb of percussion, will admit only

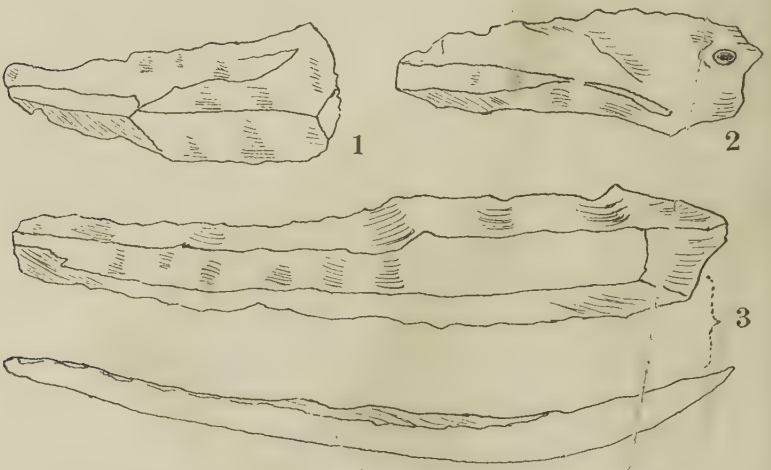

Fig. 2. Worked flakes of silica-glass. No. 2 is perforated by a hole in which a sand grain is wedged.

about 1 %. Three of these authorities agree in calling the flakes 'late neolithic or pre-dynastic'. A possible explanation of the groups of fragments found on the surface of the desert, as mentioned above, is that they were broken by human hands.

Characters and origin (L. J. Spencer).

Seven pieces of this remarkable material have been generously presented by the Survey of Egypt for the Mineral Collection of the British Museum (Natural History), and are now displayed in the Recent Addition Case in the Mineral Gallery at South Kensington, together with other material to which they appear to be most closely related, namely tektites from Bohemia, Moravia, French Indo-China, Australia, and Colombia. The masses are irregular in shape and are wind-worn on all sides (figs. 3 and 4). They range in weight

from 90·4 to 2279 grams (3¼ oz. to 5 lb.). The colour is pale greenish-yellow and the material is in part quite clear and transparent. Some parts are cloudy owing to the presence of minute bubbles, and when these are still more abundant the material has a milky white appearance. One piece shows smoke-grey streaks in the greenish-yellow glass, and indications of a flow structure are also shown in other pieces.

The clear material when cut and polished (in a step-cut form) makes quite an effective gemstone. One cut for the Museum weighs 10·57 grams (52·86 carats).[1] The specific gravity of this was determined by hydrostatic weighing to be 2·21. On the refractometer it gave the following values for the refractive index. Less reliable values were obtained by the prism method through a 60°-prism cut from the glass, owing to the scattering of the rays of light by the minute bubbles. The dispersion n_{Tl-Li} is very low.

Light.	Silica-glass, Libyan Desert.		Pure Silica-glass.[2]
	Refractometer.	Prism.	
Red (Li)	1·4595	1·459	1·45605
Yellow (Na)	1·4624	1·462	1·45845
Green (Tl)	1·4645	1·465	1·46053
n_{Tl-Li}	0·0050	0·006	0·00448

The hardness is 6 on Mohs's scale; the material readily scratches window-glass and is itself readily scratched by quartz.

In thin sections under the microscope the glass is colourless and optically isotropic. The minute bubbles do not exceed 0·1 mm. across, and the larger ones are usually collected into groups. They are round or elongated, but the direction of elongation is variable, and no indications of flow structure are seen in the sections. A very fine brownish dust pervades the whole glass, and there are a few small brown patches of irregular outline, and very few minute (0·02 mm.) black spots.

Small white spherulites, apparently due to devitrification, are occasionally present. In one specimen these are more abundant and are arranged in approximately parallel lines, like strings of small (¾ mm.) beads. They have a minutely hummocky surface, and in

[1] L. J. Spencer, Gemmologist, London, 1933, vol. 3, p. 111. [Min. Abstr., 5–398.]

[2] Values (for Li and Tl by interpolation) given by R. B. Sosman, International Critical Tables, 1929, vol. 6, p. 341.

thin section are seen to consist of a radial aggregate of comparatively coarse acicular crystals of quartz. This specimen is also peculiar in showing a clean-cut cylindrical bore completely traversing the mass of glass; it is $3\frac{1}{2}$ cm. long and 6 mm. in diameter, and approximately

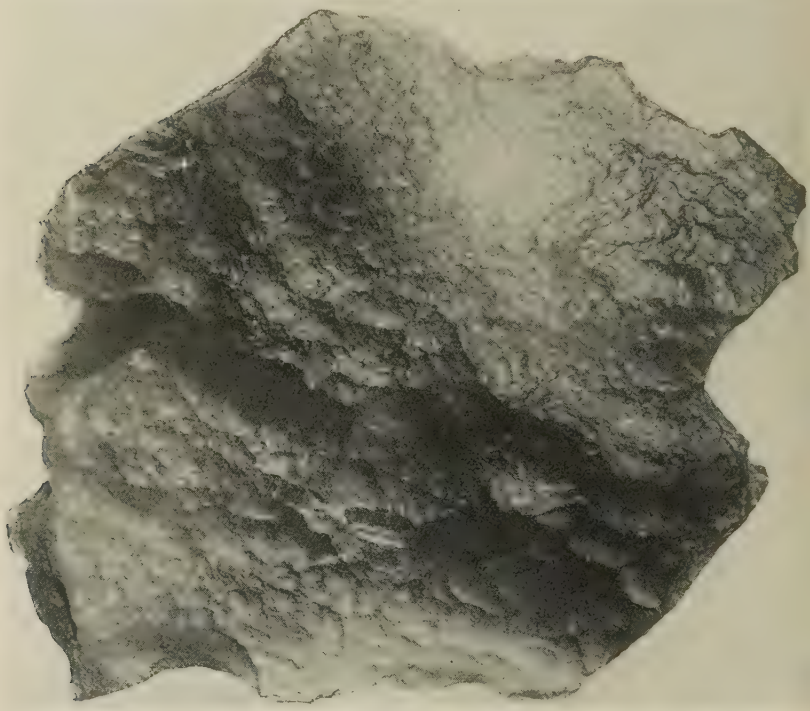

Fig. 3. Silica-glass from the Libyan Desert. Wind-worn mass of 5 lb. Half actual size.

parallel to the lines of spherulites (fig. 4). Two other such bore-holes with rounded ends penetrate for only a short distance in the same general direction. Occasionally small pits are seen on the surface of the specimens, in which a grain of sand is sometimes wedged (compare fig. 2).

The largest spherulite, $1\frac{1}{2}$ mm. in diameter, occurring alone and partly projecting from a small fragment of clear glass, afforded an opportunity of detaching a fragment for examination. This has specific gravity 2·35, and is very weakly birefringent with refractive index less than 1·49, suggesting cristobalite.

A chemical analysis of the glass made by Mr. M. H. Hey in the Museum laboratory gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	Na_2O.	H_2O.	Total.
97·58	0·21	1·54	0·11	0·23	0·38	0·34	0·10	100·49

Traces of NiO, MnO, and MgO are also present. K_2O is absent. Of the water 0·05 % was lost at 110° C., and the remainder on ignition. For the main analysis 1·0339 gram was used, and for FeO and

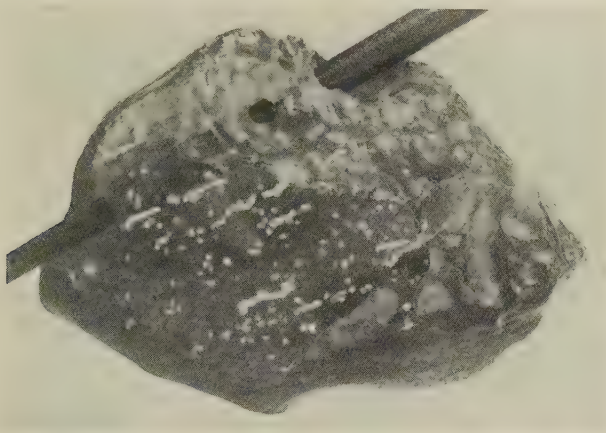

FIG. 4. Silica-glass from the Libyan Desert. Actual size. Spherulites are shown more distinctly through the flat polished surface. The rod marks a cylindrical bore which is penetrated sideways at one point. Another shorter bore with rounded end is seen towards the bottom.

alkalis separate portions of about 1 gram and ½ gram respectively. A special test was made for nickel on 2·97 grams, and the amount of NiO is probably less than 0·001 %, certainly less than 0·005. The specific gravity of the solid lump was found to be D_4^{20} $2{\cdot}206 \pm 0{\cdot}002$, and of the fine powder D_4^{20} $2{\cdot}208 \pm 0{\cdot}002$, corrected to vacuum, indicating that the bubbles present are not more than 0·6 % of the material by volume.

This silica-glass in its characters and mode of occurrence is most closely allied to tektites. But it is found in much larger masses and in larger quantity than any tektites previously known, and also it is different in colour. Tektites are usually black and in the mass opaque, but those from Bohemia and Moravia are a clear green, and small ones from Colombia are pale smoky-grey to almost colourless.

The origin of tektites is still an unsolved problem.[1] The generally accepted view at the present time is that they are of cosmic origin, but none has been actually observed to fall from the sky. The presence of silica-glass in large quantity around the meteorite craters recently discovered at Wabar in Arabia and Henbury in Central Australia, suggests that tektites may have been formed by the fusion of desert sand in the heat developed by the fall of gigantic meteorites. No evidence of this, however, has been detected in the Libyan Desert; and, moreover, the wide distribution (80×25 km.) of the material is rather against this view. Mr. Clayton remarks that from the surface geology of the district there are no indications that the material might have been transported by water, as is undoubtedly the case in the distribution of tektites.

The origin of this silica-glass on the Libyan Desert thus remains an unsolved problem. More observations are needed.

A group of craters in the Libyan Desert at about 22° 20′ N., 25° 30′ E., between Gebel 'Uweinat and Gilf Kebir, was photographed from the air by Sir Robert Clayton[2] in 1932 and was visited later in the same year by Major R. A. Bagnold's expedition.[3] They are described by Dr. K. S. Sandford[4] as explosion craters with walls of 'steeply tilted, hardened, and locally fused Nubian sandstone'. Within the craters are 'plugs of white trachytic rock and adjacent to them the fusion of the sandstone walls was very marked'. Mention is also made of an 'irony sinter'. Such a description is suggestive of meteorite craters rather than volcanic craters. Some of the silica-glass from Meteor Crater in Arizona would answer to the field description of a 'white trachytic rock', and the 'irony sinter' may perhaps be meteoritic iron-shale. 'A dark basalt-like rock of much the same specific gravity as the trachyte' is rather suggestive of the silica-glass from the meteorite craters at Henbury and Wabar. Although this locality is 200 miles to the south of the area where the lumps of clear silica-glass are found, it seems possible that there may be some connexion between the two occurrences.

[1] Nature, London, 1933, vol. 131, pp. 117, 876; vol. 132, pp. 571, 678. [Min. Abstr., 5–303, 304, 407.]

[2] Geogr. Journ., 1933, vol. 81, p. 257, and plate facing p. 252.

[3] Geogr. Journ., 1933, vol. 82, pp. 106, 215.

[4] K. S. Sandford, Volcanic craters in the Libyan Desert. Nature, London. 1933, vol. 131, pp. 46–47.

Shower of meteoric stones in the neighbourhood of the village Kuznetzovo, West Siberia, on May 26, 1932.

By Prof. Dr. P. L. Dravert (П. Л. Драверт),
Director of the Geological Section of the Bureau
for the Investigation of the Omsk region.

[Communicated by Dr. L. J. Spencer, F.R.S.; read November 9, 1933.][1]

AT the end of October 1932 information was received at the West Siberian Museum in Omsk that in May 1932 a meteorite fell in the village of Kuznetzovo (Кузнецово), 140 km. east by north from Omsk. On November 3–7, together with my assistant P. Serov, I investigated the matter on the spot. In March 1933 some further information was received, and I am now able to make the following preliminary communication.

The small village of Kuznetzovo (55° 12′ N., 75° 20′ E. of Greenwich) is situated in the western part of the Tatarsk (Татарск) district, 12 km. NE. of the Koloniya (Колония) station on the Trans-Siberian Railway. The country for a considerable distance around Kuznetzovo is level and typical of the forest-steppe zone of the West Siberian lowland.

On May 26, 1932, between 5 and 6 p.m. (local time), with the sky absolutely cloudless, a large bolide passed from west to east over the neighbourhood of Kuznetzovo. Its passage was accompanied by a buzzing noise which lasted for some time and resembled the sound of a flying aeroplane. Then were heard at short intervals deafening detonations resembling the firing of big guns. Some people counted ten detonations, others heard fewer. In the sky there appeared a small dark cloud with three times the apparent diameter of the moon, and several stones fell on the surface of the earth. The front part of the air-wave produced by the passage of the meteorite caused a brief whirlwind which rocked the tops of birch trees in a small wood near the village. It was also noted that the ground shook, window-panes rattled, and hanging articles began to swing.

[1] Translated from the Russian typescript by B. P. Uvarov, Department of Entomology, British Museum of Natural History.

Sounds resembling the firing of guns were heard in the villages Ivanovka (Ивановка), Medvezhya Griva (Медвежья Грива), Ermolaevka (Ермолаевка), Dmitrievka (Дмитриевка), and others within a radius of 20 km. In the village of Orlovo (Орлово), 20 km. to the west of Kuznetzovo, a black streak was observed in the sky moving eastwards.

On the south-eastern margin of the village of Kuznetzovo the fall of one stone was witnessed by a boy Michael Ivanov, eleven years of age, and his mother Natalya, who was working in her vegetable

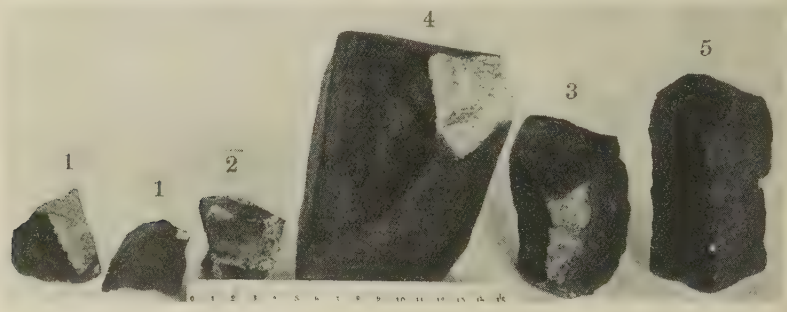

Fig. 1. Group of stones recovered from the Kuznetzovo shower. (Scale of centimetres.)

garden. They saw a black object flying towards them, rotating in the air, and making a whistling noise. When it came nearer it made, according to the boy, a noise ' like two million rising pigeons ' ; his mother said ' like many large birds '. This stone (no. 1) fell two metres from the place where the small children of the Ivanov family were playing. It made a small oblique hole in the ground and then rebounded for a distance of 17 cm. The grass in the hole was scorched, and the meteorite was still warm when picked up ten minutes later. It weighed 2 kilograms.

Stones nos. 2, 3, 5, and 6 were found on the second and third days after the fall in the same south-eastern part of the village. No. 4 was found in the steppe near the farm Sladkoe (Сладкое), 3 km. NE. of the village, only because a horse had stumbled against it. According to later information two more stones were found in Kuznetzovo; no. 7 weighing about $\frac{1}{2}$ kg. and no. 8 weighing about 16 kg. In addition to these it is rumoured that ' many stones have been found '. It is quite possible that other stones have been found and hidden by the inhabitants of the village, and that some have

fallen and remained buried in the ground in the steppe outside the boundary of the village.

The peasants of Kuznetzovo did not regard the stones fallen from the sky with any superstitious awe, although they were alarmed by the unexpected and rare phenomenon. They dealt with them in a practical manner; and mistaking the inclusions of troilite for gold,

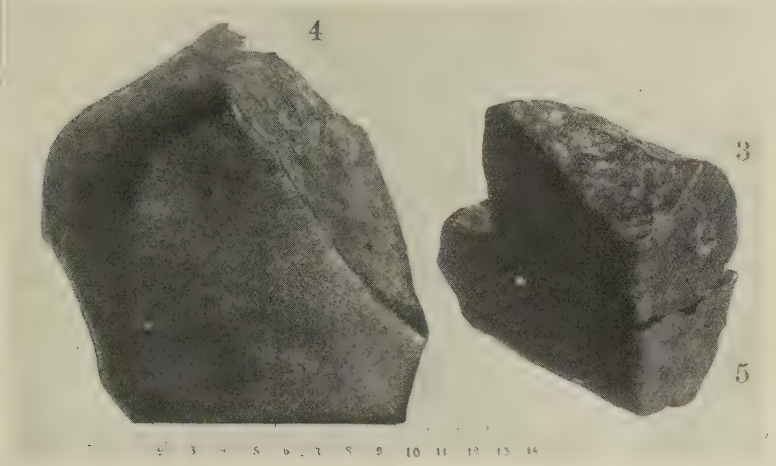

FIG. 2. Another view of the three larger stones recovered from the Kuznetzovo shower, showing nos. 3 and 5 fitted together. (Scale of centimetres.)

they heated the stones in the fire, ground them to powder, and washed in water to obtain the gold, but without success.

We succeeded in bringing to Omsk from Kuznetzovo three complete stones only slightly damaged, namely nos. 3, 4, and 5, weighing 547·2, 2538, and 655 grams respectively; two fragments of no. 1 weighing 99·05 and 75·95 grams; and fragments of no. 2 weighing 132·2 grams, a total of 4047·4 grams (fig. 1).

According to my estimate from the data obtained the total weight of the eight known stones is about 23 kg. But, as mentioned above, some stones may have remained with the peasants or buried in the ground; and therefore this weight must be regarded as a minimum for the whole shower. Even so the Kuznetzovo meteorite is the largest stony meteorite that has been observed to fall in Siberia.

The Kuznetzovo stones in our possession are irregular polyhedra, bounded either by more or less flat or by curved surfaces, which meet in sharp or somewhat rounded edges. The surfaces are marked

by pits (' piezoglypts ') of unequal size and varying form. Each stone has one prominently flat surface without any noticeable pits, a feature which appears to be of some significance. Stones nos. 3 and 5, which fell about 330 metres apart, fit together on their flat crusted surfaces (fig. 2). Apparently these, as well as some of the other pieces, formed part of one cosmic mass, which was broken up on entering the earth's atmosphere. This is similar to the Butsura meteorite (fell in India on May 12, 1861) the pieces of which could be fitted together.

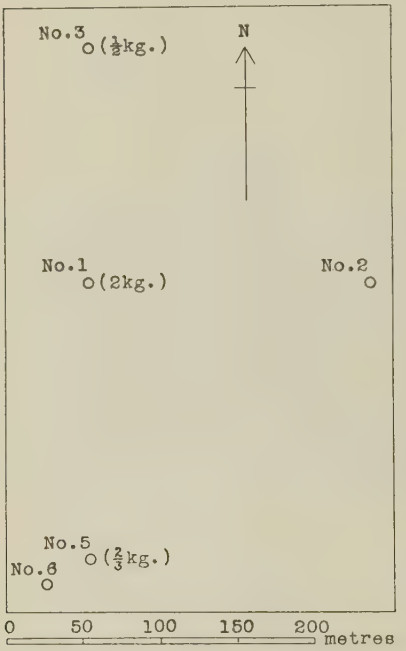

Fig. 3. Distribution of stones found in the SE. portion of the village of Kuznetzovo. [No. 4 (2½ kg.) was found at a distance of 3 km. to the NE. The positions of nos. 7 and 8 not known.]

The stones are covered with a thin dull black crust. Over this primary crust a secondary crust may be distinguished with a lens on most of the surfaces. This is lighter in colour, bubbly and slaggy with reticulated markings, and in places streaky with small drop-like formations. On stone no. 4 one surface has a blackish-brown crust; and the dull black crust on the large flat surface shows several silver-white grains (1 mm. and less) of nickel-iron. On stone no. 1 the crust inside a pit is dark greenish-grey with a shining glassy surface.

The material of the stones is greyish-white, friable, and fine-grained. It shows minute chondrules of olivine and occasional small balls (up to 2 mm.) apparently of bronzite. Numerous small yellow inclusions of troilite are scattered through the mass. The specific gravity of the 99·05-gram portion of stone no. 1 was determined by hydrostatic weighing to be 3·52.

Progressive metasomatism in the flint nodules of the Scawt Hill contact-zone.

(With Plate XXI.)

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[Read November 9, 1933.]

IN describing the chief assemblages of the Scawt Hill contact-zone in Co. Antrim brief reference was made to the occurrence of wollastonite and xonotlite associated with the flint nodules of the contact-altered chalk.[1] A more detailed examination of these nodules has now been made and the study of a large number of examples has revealed an interesting group of mineral assemblages which have developed by a progressive metasomatism of these siliceous bodies.

The nodules, despite the fundamental mineral changes which have affected them, can be readily recognized in the contact-zone retaining as they do the characteristic form of the original nodule and being sharply demarcated from the larnite-spurrite-rocks by which they are encased. Where the metasomatism is more intense as the junction is approached, the larnite-rock in the vicinity of the nodules tends to become in some examples—not in all—darker, due to an increase in the spinel or magnetite content. A Liesegang effect is sometimes produced by the development of a series of roughly concentric rings in which is found an increase in dark mineral content (spinel and magnetite). Three types of altered nodules may be distinguished, but all three are connected by gradational varieties.

Type *a*.—Where little metasomatism is involved the principal metamorphic effects are seen in a recrystallization of the chalcedony to granular quartz, while the immediate boundary against the larnite-rock is a narrow sheath of fine-grained wollastonite. At this stage migration of lime has usually begun and the nodule is veined by narrow stringers consisting of wollastonite crystals. Smaller crystals are also found enclosed in and interstitially among the quartz grains.

[1] C. E. Tilley, Min. Mag., 1931, vol. 22, pp. 443–444.

This is a case of pure lime metasomatism demanding nothing more than migration from solutions inherent in the limestone originally encasing the nodules.

Type *b*.—A more fundamental change is revealed in other types of nodules which, when broken open, reveal a peripheral greenish ring gradually encroaching towards the white centre of the nodule. In the large nodules various stages of partial to complete replacement can be studied. Examination of the greenish zone shows it to be composite and made up largely of a fine-grained sheaf of fibres in which are set clear pearly laths of wollastonite ranging in size up to 15×1 mm.

Where the metasomatism is incomplete the core of the nodule is built up of quartz grains enclosing and interstitially surrounded by the same fibrous material which forms the bulk of the green periphery. This passes out—usually rapidly—into the green zone in which practically all quartz has disappeared. Ultimately in the case of the smaller nodules the whole is converted into a green coloured assemblage in which porphyroblasts of wollastonite can be readily recognized by the unaided eye.

Under the microscope the green zones are seen to be built up of divergent sheaves of xonotlite surrounding porphyroblasts of wollastonite. These xonotlite sheaves vary in colour from point to point. Some are practically colourless, whilst others are of a distinct green tint and are pleochroic. The colourless xonotlite has already been noticed forming fibres elongated along γ with straight extinction. In cross-section the bundles give 2V very small, sensibly uniaxial, and positive; refractive indices somewhat variable but average α 1·578, γ 1·590. Between the colourless fibres and others distinctly green and pleochroic there are all gradations. The markedly green variety has γ green, α lighter green to light brown-green. The similarity in orientation and the gradation the fibres exhibit in refraction, double refraction, and colour indicate that the colour is due essentially to replacement by ferrous iron.

The wollastonite laths have the usual habit elongated along the *b*-axis with prominent (100) faces, and twinning on (100). Outgrowths of xonotlite from the wollastonite laths are frequently developed.

At this stage there is an incipient development of a greenish monoclinic pyroxene found amongst the felt of xonotlite fibres and exceptionally appearing even in small porphyroblasts as green

hedenbergitic diopside. In some examples aegirine occurs as fine fibres in the same fashion.

These constituents make up the greater part of the green zones, but sporadically developed are found small areas or nests filled with colourless fibrous okenite, often associated with recrystallized quartz. The okenite has the optical properties of that described by Bøggild.[1] The extinction of the fibres while frequently parallel shows in different fibres values up to 30°, confirming the low symmetry which Bøggild has already indicated. Elongation positive, 2V large, and the sign is negative though this is not readily determined. The refraction is less than that of quartz γ 1·540 and the double refraction like that of the associated quartz 0·009. These properties identify the mineral with okenite. Nevertheless in some sections the refraction of otherwise similar material is somewhat greater, reaching a figure of γ 1·553. Material corresponding to this value is recorded for okenite by Lacroix.[2] Whether this variation is due to variable water content is not known, but it is clear that a systematic examination of okenite, in view of the discrepancies in the data that appear in the literature, is required.

An analysis of a nodule of type *b* is given on p. 517. It reveals a surprising content of soda, which from the microscopic features is unexpected. The wollastonite fibres were separated from the rock, and the fibrous material which is almost wholly xonotlite, but still containing a small percentage of pyroxene fibres and a little okenite and quartz which it was impossible to separate from the felt, gave on partial analysis SiO_2 50·45, $(Al,Fe)_2O_3$ (all Fe determined as Fe_2O_3) 5·66, CaO 27·94, Na_2O 4·41, K_2O 0·82, MgO n.d., H_2O 7·41 %. It is clear that the bulk of this soda must be present in the xonotlite which has also a high water content comparable with the figure given by Shannon for the Leesburg xonotlite.[3] Part of it is no doubt water adsorbed on the surface of the fine fibres.

In its soda content the xonotlite is most comparable to the natroxonotlite described by Williams from the Potash Sulphur Springs region, Arkansas,[4] which has CaO 36·72, Na_2O 4·41 %. The greenish

[1] O. B. Bøggild, Kgl. Danske Vidensk. Selsk. Mat.-fys. Meddel., 1922, vol. 4, no. 8, pp. 15–16. [Min. Abstr., 2–59.]

[2] A. Lacroix, Bull. Soc. Min. France, 1885, vol. 8, p. 341; 1887, vol. 10, p. 316.

[3] E. V. Shannon, Proc. United States National Museum, 1925, vol. 66, art. 28, p. 12. [Min. Abstr., 3–204.]

[4] J. F. Williams, Annual Report Geol. Survey Arkansas, 1891, vol 2 (for 1890), p. 356.

colour of much of the xonotlite of Scawt Hill must be ascribed to ferrous iron which with sodium is replacing the calcium of the pure lime-xonotlite.

Type *c*.—A still more fundamental metasomatism is revealed in certain other nodules which are less abundantly developed. Here again the form of the characteristic flint nodule is preserved. These nodules are distinguished by their coarse grain size and abundant wollastonite. As compared with the nodules already described the areas intervening between the wollastonite nodules are much darker in colour and built up of coarser grained material. The clear pearly wollastonites reach up to 25×10 mm. in size and are frequently sheathed by a fibrous alteration product.

Under the microscope the dark areas between the wollastonite blades are seen to be composed of a strongly zoned pyroxene as relatively large crystals up to 3 mm., and less abundant melilite. The sheath around the wollastonite blades is seen to consist of pectolite partly in parallel growth and extending along the cleavages, but passing out into divergent fibres of the same mineral.

The pectolite is characterized by its high double refraction, α 1·597, γ 1·633, uniform positive elongation and sign. The parallel growth of the pectolite around the wollastonite is revealed not only in the longitudinal but also in the cross-sections, the (100) and (001) cleavages of the wollastonite passing into the narrow mantle of pectolite which in this orientation has the acute bisectrix (γ) emerging from the section. The pectolite is clearly developing from the wollastonite and in some cases the wollastonite forms a mere residual in an aggregate of pectolite fibres.

The pyroxenes of the nodule are characteristically strongly zoned and in various nodules range from green augite through aegirine-augite to aegirine, the last of which may form separate crystals or as a peripheral zone to the green augite or aegirine-augite. The pleochroic scheme of the aegirine is γ brown, β brown-green, α grass-green. The aegirine-augite is pleochroic in the same tints, but less strongly marked. The aegirine itself appears to pass out in places to an acmite of brown tint with but feeble pleochroism.

The melilite has the features characteristic of this mineral in the hybrid zone,[1] but it is now in various stages of replacement, principally by magnetite, which develops thickly along the cleavages and fractures. Among the birefringent felt of fibres simultaneously

[1] C. E. Tilley, loc. cit., p. 455.

developed with the magnetite is cebollite, with other fibres of indeterminate character owing to the fine confused texture, which does not permit unravelling of their optical properties. In addition to occurring as a replacement of melilite, magnetite also occurs interstitially among the pyroxenes, while there is usually a small amount of pyrrhotine associated with it. Small nests of okenite like those already described are also found, but xonotlite is typically absent.

The profound metasomatism which the flint nodules have experienced render chemical analyses of these assemblages instructive. Two such analyses executed on material of type *b* and type *c* are set down below, together with a previously recorded analysis of a metasomatized chalk rock.

	I.	II.	III.
SiO_2	51·57	42·58	22·52
TiO_2	0·14	0·61	0·57
Al_2O_3	1·10	2·73	10·11
Fe_2O_3	1·85	4·29	4·58
FeO	2·17	4·77	2·90
MnO	0·42	0·68	—
MgO	0·94	2·27	4·93
CaO	30·25	32·93	46·36
BaO	0·15	0·22	—
Na_2O	3·59	2·67	1·06
K_2O	0·52	0·20	0·05
H_2O+ ...	5·66	5·03	0·78
H_2O- ...	1·10	0·19	0·08
P_2O_5	n.d.	0·05	0·19
CO_2	0·56	0·55	5·08
Cr_2O_3	nil	nil	—
S	0·14	0·49	0·49 (SO_3)
			0·18 (FeS)
	100·16	100·26	99·88
Fe/Mg ...	5·3	4·9	1·8
Sp. gr. ...	2·69	2·92	—

I. Xonotlite-wollastonite-rock (type *b*).

II. Wollastonite-pyroxene-melilite-rock (type *c*).

III. Metasomatized chalk (spurrite-merwinite-gehlenite-spinel-(calcite)-rock). Min. Mag., 1931, vol. 22, p. 445.

The first two analyses show that from the incoming solutions the chief constituents replacing the silica of the flint nodule are CaO—for which the source is largely the encasing limestone, —Na_2O, and iron oxides. These have been selectively absorbed and partook of reaction with SiO_2 to form the constituent minerals. Alumina, which in the metasomatized chalk is often abundantly precipitated

in the form of spinel and gehlenite, plays here a subordinate role and is only significantly represented in type *c* where it appears in the form of melilite.

The preservation of the characteristic shape and form of the flint nodules—sharply marked off from the surrounding limestone—renders these metasomatic assemblages particularly convincing examples of a replacement process unaccompanied by volume change. It is indeed a striking case of the rule of equality of volume, a thesis which Lindgren [1] has repeatedly urged for metasomatism. The incoming of CaO, Na_2O, iron oxides, and water has been accompanied by an outward migration of silica. Comparing the specific gravities of the original flint nodule (2·65) and a rock of type *c* (2·92) it is readily seen that for every 100 c.c. of flint nodule involved there has been an effective outward migration of 140 grams of silica, which has no doubt played its part in the silication of the carbonate casing.

Explanation of Plate XXI.

Fig. 1. Flint nodule (partly metasomatized) in larnite-spurrite-spinel-rock. Scawt Hill, Larne, Co. Antrim. $\times\frac{4}{5}$.

Fig. 2. Section through metasomatized flint nodule. Scawt Hill. The interior of the flint nodule has at this stage suffered little change and consists of a fine-grained quartz aggregate. The interior zone passes rapidly into a coarser zone built of quartz with interstitial soda-xonotlite, and this zone again into the peripheral zone consisting essentially of wollastonite (clear areas) and fibrous radiating nests of brown to greenish soda-xonotlite. ×16.

[1] W. Lindgren, Bull. Geol. Soc. America, 1925, vol. 36, p. 247.

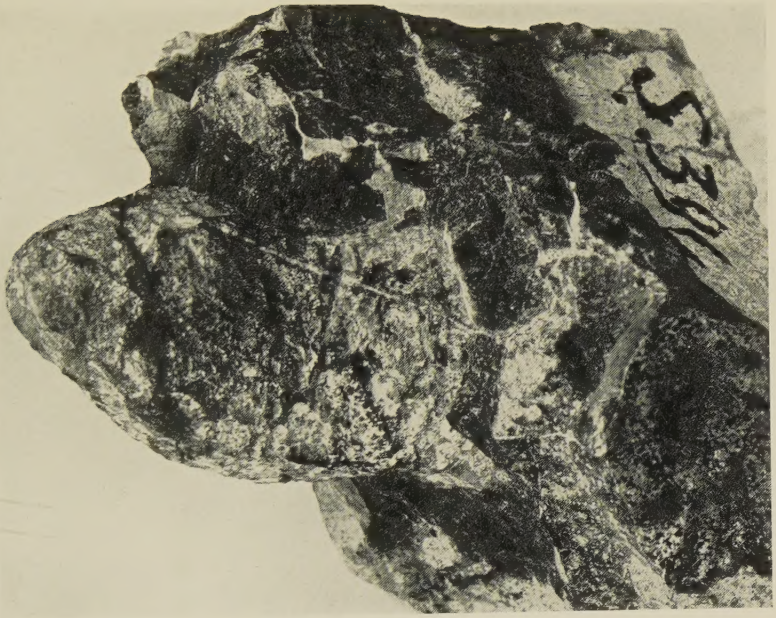

Fig. 1.

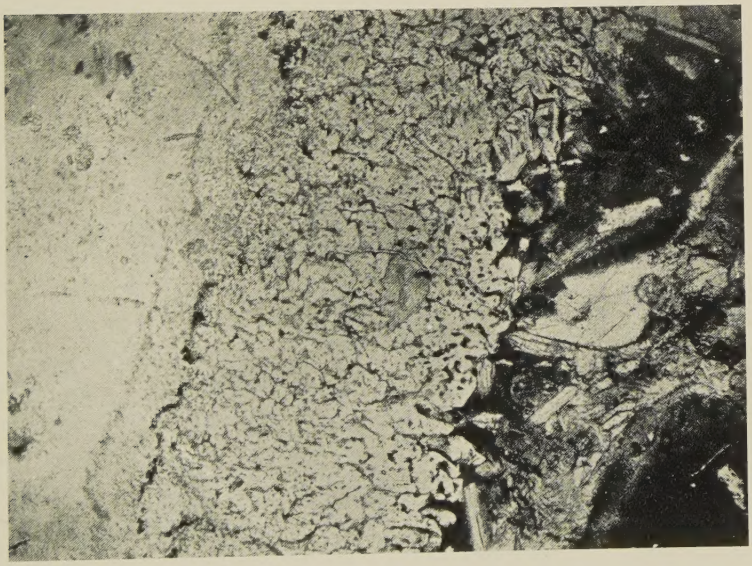

Fig. 2.

C. E. Tilley and A. R. Alderman: Metasomatism of Flint Nodule.